



Full Length Article

Enhancement of sulfur and nitrogen removal from heavy gas oil by using polymeric adsorbent followed by hydrotreatment

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ABSTRACT

This study is focused on the challenges associated with the utilization of heavy oil as refinery feedstock. Various catalytic and non-catalytic methods to achieve higher desulfurization of feed have been widely studied in the past. In this study, we are proposing a new integrated technology that combines selective adsorption of heterocyclic sulfur and nitrogen compounds followed by catalytic hydrotreatment. Glycidyl methacrylate based polymers were developed in bulk and used as an adsorbent for the removal of nitrogen and sulfur species. In the first step, the polymeric adsorbent reduced sulfur and nitrogen content of heavy gas oil through charge transfer complex formation. Optimization of adsorption parameters was done using Taguchi orthogonal array to maximize the removal of catalyst inhibiting nitrogen heterocyclic compounds. Afterwards, hydrotreatment of polymer treated heavy gas oil was studied in a trickle-bed reactor. Functionalized polymer treated feed was hydrotreated using NiMo/γ-Al₂O₃ catalyst synthesized in lab with 13 wt% molybdenum and 2.5 wt% nickel, and hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodearomatization (HDA) activities were measured. Experiments were performed in the temperature range of 370–390 °C, pressure of 8.96 MPa, 1 h⁻¹ LHSV and H₂/oil ratio = 600 (v/v). Prior removal of nitrogen and sulfur compounds using functionalized polymer subsequently favored the hydrotreating activity in the trickle bed reactor. Removal of refractory sulfur and nitrogen species before hydrotreatment has resulted in 94.3 wt% HDS and 63.3 wt% HDN as compared to 93.1 wt% HDS and 60.5 wt% HDN activities at optimum temperature of 390 °C. A total of 42.8% aromatic content was found in untreated HGO which decreased in the polymer pre-treated HGO. The highest HDA was observed for polymer pre-treated HGO feed at 390 °C, where the aromatic content decreased from 23.9% to 21%.

1. Introduction

Global energy consumption is increasing significantly due to the rapid economic growth and expanding population in developing countries. U.S. Energy Information Administration (EIA) reported a 48% increase in total world consumption of energy from 2012 to 2040. In 2012, transportation sector accounted for 25% of total world energy consumption. It is expected to increase at a rate of 1.4%/year from 2012 to 2040 [1]. Liquid fuels, natural gas, and coal are the fossil fuel resources exploited to meet the increasing energy demand. However, adverse environmental effects of fossil fuel emissions is a major concern worldwide. Crude oil is one of the major energy sources used in transportation and industrial sector. Heavy oil or synthetic oil derived from oil sands is one of the alternative source of liquid fuels. Natural Resources Canada has reported that Canada has the world's third largest (10.3%) proven oil resources which can be recovered with the

existing technological conditions. Canada accounts for 171 billion barrels of proven oil reserves, out of which 166.3 billion barrels is present in the form of oil sands [2]. Bitumen is a heavy and unconventional form of crude oil derived from oil sands, containing a large amount of middle distillates as compared to the conventional crude oil. Bitumen derived heavy oil is a mixture of hydrocarbons, organic compounds such as sulfur, nitrogen, and metals such as vanadium, nickel, copper and iron. It is usually characterized by high viscosity, low API gravity, low hydrogen to carbon ratio and high content of metals, sulfur, and nitrogen.

Concentration of nitrogen and sulfur compounds in crude oil varies depending upon the initial and final temperatures of distillation, and the nature and origin of crude oil. Bitumen-derived heavy gas oil (HGO) contains high sulfur and nitrogen content present predominantly as heterocyclic aromatic compounds which makes the hydrotreating processes challenging. Pyridine, quinoline, indole, carbazole and its

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derivatives are the examples of nitrogen impurities found in HGO. Thiols, sulfides and disulfides, thiophenes, benzothiophenes, dibenzothiophenes are the major sulfur compounds present in gas oil. Heavy oils contain ≥ 3 -ring polycyclic sulfur compounds, including dibenzothiophene and its alkyl-substituted derivatives such as, 4-methylthiophene and 4,6-dimethylthiophene [3]. These thiophenic compounds are least reactive and difficult to remove during hydrotreating process.

Hydrotreating is a vital part of oil refining process involving catalytic reactions in the presence of hydrogen at elevated temperatures (350–400 °C) and elevated pressures (8–10 MPa) to fulfill the following objectives [4]: (a) Removal of hetero-atoms such as S and N from crude oil, (b) Improvement of FCC feedstock quality due to lower sulfur content, (c) Hydrogenation of aromatics, (d) Improvement of stability of the final feedstock for storage, and (e) Removal of heavy metals, such as Vanadium and Nickel. Alumina supported Mo- and W-based sulfides with promoters of Ni and Co sulfides are highly favored hydrotreating catalysts in industries. Cobalt-promoted Mo/ γ -Al₂O₃ is preferred for hydrodesulfurization, while use of nickel is favored for hydrodenitrogenation reactions. Additives, such as phosphorus and boron are also widely applied to increase the hydrotreating activity. During the hydrotreating process, removal of sulfur (hydrodesulfurization, HDS) and removal of nitrogen (hydrodenitrogenation, HDN) heteroatoms takes place in the form of hydrogen sulfide and ammonia, respectively and saturation of aromatics (hydrodearomatization, HDA) occurs simultaneously.

Approaches to ultra-deep HDS include the removal of refractory thiophenic compounds and their derivatives, particularly 4,6-DMDBT [5]. Nitrogen compounds naturally occurring in gas oil are one of the strongest HDS inhibitors and extensive amount of work has been done to study their inhibition and removal. Upon achieving high desulfurization activity, when the amount of refractory sulfur compounds is very low then the polyaromatics and nitrogen compounds present in feed inhibit the HDS conversion through competitive adsorption [6]. To prove the usefulness of nitrogen removal and to evaluate the effects of its concentration in gas oil, Choi et al. [7] studied HDS reactions using conventional straight run gas oil (SRGO) and its denitrogenated gas oils. Hydrotreating at 340 °C reduced the total sulfur content from 14354 ppm to 19 ppm and 120 ppm for 80% and 64% denitrogenated gas oil, respectively. Whereas, a high sulfur content (311 ppm) was detected after hydrotreating of untreated SRGO under same conditions. Laredo et al. [8] described that the inhibiting effects of non-basic nitrogen compounds, indole and carbazole on HDS of dibenzothiophene were comparable to that of the basic nitrogen compound, quinoline. The inhibition increases in the order: carbazole < quinoline < indole. They also reported that the inhibiting effects of individual nitrogen compounds were very strong, even at concentrations as low as 5 ppm. Tao et al. [9] studied the inhibiting effects of quinoline and indole on hydrodesulfurization of thiophenic compounds present in straight-run gas oil. It was found that the inhibiting effect of quinoline on HDS of gas oil is higher as compared to indole. By increasing N/S concentration in the feed, a significant inhibition was observed in HDS activity. The HDS of refractory sulfur compounds (dibenzothiophene and its derivatives) was strongly inhibited by the increase in nitrogen concentration, while the HDS of thiophene and benzothiophene was slightly inhibited. In order to improve the efficiency of the hydrotreating process, two main routes can be followed: one is the removal of refractory sulfur compounds, such as 4,6-DMDBT and another is the removal of HDS inhibitors such as pyridine, acridine, carbazole and its derivatives before hydrotreating.

Non-catalytic processes such as, activated carbon, zeolites, ion exchange resin, metal organic framework and π -acceptor functionalized polymers have shown promising results in the removal of heterocyclic nitrogen and sulfur compounds from various petroleum feedstocks [10–16]. Aromatic nitrogen and sulfur heterocyclic compounds are electron rich (π -donors) and when contacted with electron deficient (π -

acceptors) species lead to the formation of charge transfer complexes and their consequent removal from the feed. Sevignon et al. [17] successfully removed 23% of the total sulfur from Straight Run oil (SR) using poly(styrene) functionalized polymer. Macaud et al. [18] investigated the removal of non-basic nitrogen compounds from SR oil via charge transfer complex formation and observed a 60 wt% decrease in the nitrogen concentration by using a functionalized hydrophilic support.

Based on the available literature it was found that the following approaches may lead to deep HDS of gas oil: (a) Development of new catalysts with more active sites [19,20], or (b) Removing catalyst inhibitors from gas oil using adsorbents before hydrotreating [7,21]. This work is focused on the second approach of enhancing the efficiency of hydrotreating processes by removing nitrogen species from bitumen-derived heavy gas oil (HGO). A feed pre-treatment process using functionalized polymers has been developed for the selective removal of heterocyclic nitrogen compounds from HGO by the formation of charge transfer complexes. It was followed by hydrotreatment of both untreated HGO and pre-treated HGO feed to measure the effects of presence or absence of nitrogen species on hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activities at industrial hydrotreating conditions.

2. Experimental details and methodology

2.1. Materials

Mo and Ni precursors, ammonium heptamolybdate tetrahydrate (AHM) ((NH₄)₆Mo₇O₂₄·4H₂O) and nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O); monomers, glycidyl methacrylate and ethylene glycol dimethacrylate; 1-dodecanol ($\geq 98.0\%$), cyclohexanol (99.0%), N,N-dimethylformamide (anhydrous 99.8%), poly[N-vinyl-2-pyrrolidone] (Mw ~ 55,000 g/mol), acetone oxime ($\geq 98.0\%$), potassium carbonate ($\geq 99.0\%$), 9-fluorenone (98%), fuming nitric acid (90%) and p-toluene sulfonic acid monohydrate ($\geq 98.5\%$) were purchased from Sigma Aldrich, Edmonton, Canada. Azobisisobutyronitrile was purchased from Molekula Ltd. Ammonium hydroxide (28–30% NH₃ in water), sulfuric acid (95–98%) and the γ -Al₂O₃, which was used as a support for catalyst were purchased from Fischer Scientific, Saskatoon, Canada. Heavy gas oil was provided by Syncrude Canada Ltd. All the chemicals were used without further purification.

2.2. Catalyst preparation

The NiMo/ γ -Al₂O₃ catalyst was synthesized using wetness sequential impregnation method. 13 wt% Mo and 2.5 wt% Ni was loaded on γ -Al₂O₃ using (NH₄)₆Mo₇O₂₄·4H₂O and Ni(NO₃)₂·6H₂O as precursors. In a typical synthesis, 2.4 g of AHM was dissolved in 10 mL of water containing few drops of ammonium hydroxide. The resulting solution was impregnated on 8.45 g of γ -Al₂O₃. The material was then dried for 6 h at 110 °C followed by calcination at 550 °C for 5 h at a ramp rate of 1 °C/min. To this material, solution of 1.24 g nickel nitrate in 7 mL water was wet impregnated. The resultant material was dried for 6 h at 110 °C followed by calcination at 550 °C for 5 h at a ramp rate of 1 °C/min to produce 10 g of NiMo/ γ -Al₂O₃ catalyst.

2.3. Preparation of functionalized polymer

Functionalized polymer consisting of a polymer support, copolymer of glycidyl methacrylate and ethylene glycol dimethacrylate (PGMA), a fluorenone derived π -acceptor with four nitro groups (2, 4, 5, 7-tetra-nitrofluorenone, TENF), and a hydroxylamine linker, was synthesized to create PGMA-ON-TENF polymer. The epoxy group present on PGMA support was opened to attach the linker. Thereafter, the π -acceptor was immobilized on the polymer support via hydroxylamine linker. Detailed synthesis of PGMA and TENF, and the procedure for obtaining

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